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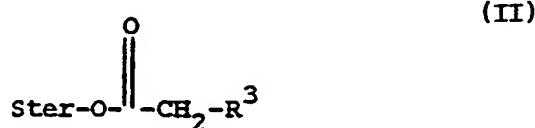
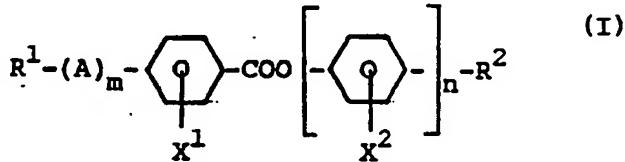
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(54) Title: DECORATIVE COMPOSITION



(57) Abstract

New decorative compositions which contain non-chiral compounds of formula (I), and chiral steroid esters of formula (II), wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, A, X<sup>1</sup>, X<sup>2</sup>, Ster, m, and n have the meaning given in Claim 1.

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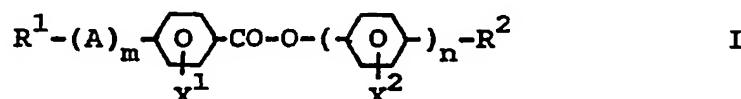
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### Decorative Composition

The application relates to a decorative composition comprising in admixture:

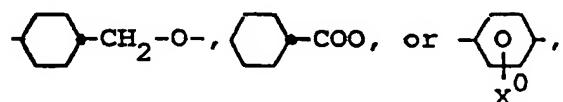
- a) one or more non-chiral compound of the  
5 formula I



wherein

R<sup>1</sup> and R<sup>2</sup> are each independently a normal or  
10 branched alkyl or alkenyl residue  
with up to 16 C atoms wherein one  
or two nonadjacent CH<sub>2</sub> groups of  
these residues may be replaced by  
-O- or -CO-

15 A denotes a group of the formula



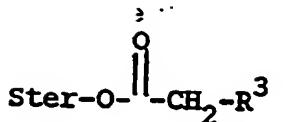
x<sup>0</sup>, x<sup>1</sup> and x<sup>2</sup> are each independently hydrogen or  
an halogen atom,

20 m is 0 or 1, and

n is 1 or 2,

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- b) one or more chiral steroid ester of the formula II



II

wherein

5         $\text{R}^3$         is a normal or branched alkyl or  
                alkenyl residue with up to 16 C atoms  
                wherein one  $\text{CH}_2$  group may be replaced  
                by  $-\text{O}-$ ,  $-\text{O}-\text{CO}-$  or  $-\text{CO}-\text{O}-$ , and

10        Ster        denotes a saturated or unsaturated  
                gonan-3-yl group being optionally sub-  
                stituted by up to 6 normal or branched  
                alkyl residues with 1 to 10 C atoms,  
                and

c) at least one vehicle and, if desired, at least  
15        one auxiliary.

For decorative applications, particularly in cosmetics there is a need for new colour effects which impart to the formulations an advantageous appearance and contain physiologically acceptable dyestuffs permitted in cosmetics.

20        However, in addition to the coloured gloss and the aesthetic effects achieved with this, the behaviour of the formulation on the skin, the so-called "feeling", also plays a decisive role in cosmetic formulations. The known cosmetic pigments are still in need of improvement in this respect.

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It is known that compositions containing p-alkyl-(or p-alkoxy)phenyl p-alkyl-(or p-alkoxy)benzoates and an optically active cholesteryl ester are suitable for temperature indicating devices, the British Patent  
5 Specification 1583137 and 1583137 describe compositions containing, for example, cholesteryl oleate, p-pentyl-phenyl-p-pentyloxybenzoate and p-pentylphenyl-p-methoxybenzoate and being useful as temperature indicating compositions. But there is no hint that such compositions  
10 can be used as decorative compositions.

It is now been found, surprisingly, that when decorative compositions being an admixture of compounds of the formula I, chiral steroid esters of the formula II, vehicles and optionally auxiliaries are used in cosmetic  
15 formulations, particularly skin-friendly pleasant preparations are obtained, and very aesthetic effects can also be achieved by the metallic coloured gloss.

The invention therefore relates to decorative compositions comprising an admixture of at least one non-chiral compound of the formula I, at least one chiral steroid ester of the formula II and at least one vehicle and, if desired, at least one auxiliary.  
20

Liquid crystal phases are exhibited by certain organic compounds and constitute an intermediate state which  
25 exists between the crystalline solid and the fully disordered liquid phase and within which certain long range ordering of the molecules takes place.

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There are two important types of liquid crystal phase; the smectic mesophase in which the long range ordering is of a substantially lamellar type and the nematic mesophase in which the ordering is substantially linear,  
5 i.e. the molecules tend to line up with the long axes of the molecules parallel.

Included sometimes as a subclass of the nematic mesophase and sometimes classified as a separate mesophase is the cholesteric mesophase. This last has a helical long  
10 range order imposed upon the linear order of the nematic mesophase. Compounds displaying a cholesteric mesophase are optically active (chiral) and the pitch of the helical twist is determined by the nature and extent of the optical activity. The pitch of the helical twist may  
15 be such that thin films of the cholesteric phase reflect visible light, resulting in the observation of bright colours.

The chiral steroid esters of the formula II induce a cholesteric mesophase (hereinafter designated Ch)  
20 because of their molecular shape and optical activity to the liquid crystalline composition containing the compounds of the formula I which possess a nematic mesophase. As a result of these properties, the compositions according to the invention have not only a high refractive  
25 index and high gloss but also a very good skin feeling.

The compounds of the formula I used according to the invention are known per se and have also already been proposed as components for liquid crystalline compositions which can be applied in electro-optical display devices

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- or in temperature indicating devices. Processes for their preparation are described, for example, by R. Steinsträsser, Z. Naturforsch. 27b, 774 (1972), German Patent Application 2240864, U.S. Patent 4,136,053 or the British Patent 5 Applications 8800800, 8800801 and 88 11 374 and other publications quoted in the literature mentioned above.

Above and below  $R^1$ ,  $R^2$ ,  $R^3$ , A,  $X^0$ ,  $X^1$  and  $X^2$ , m and n have the meaning given, unless expressly indicated otherwise.

- 10 Phe denotes a 1,4-phenylen group, PheX denotes a 1,4-phenylen group substituted by an halogen atom and Cy denotes a trans-1,4-cyclohexylen group.

- The compounds of the formula I accordingly include preferred compounds with two rings of the part formulae Ia to Id:

$R^1$ -Phe-COO-Phe- $R^2$	Ia
$R^1$ -PheX-COO-Phe- $R^2$	Ib
$R^1$ -Phe-COO-Phe- $R^2$	Ic
$R^1$ -PheX-COO-PheX- $R^2$	Id

- 20 compounds with three rings of the part formulae Ie to Il

$R^1$ -PhePhe-COO-Phe- $R^2$	Ie
$R^1$ -PheX-Phe-COO-Phe- $R^2$	If
$R^1$ -Phe-Phe-COO-PheX- $R^2$	Ig
$R^1$ -Phe-COO-PhePhe- $R^2$	Ih
25 $R^1$ -Cyc-CH <sub>2</sub> O-Phe-COO-Phe- $R^1$	Ii
$R^1$ -Cyc-COO-Phe-COO-Phe- $R^2$	Ij
$R^1$ -Cyc-CH <sub>2</sub> O-PheX-COO-Phe- $R^2$	Ik
$R^1$ Cyc-CH <sub>2</sub> O-Phe-COO-PheX- $R^2$	Il

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and compounds with four rings of the part formulae I<sub>m</sub> to I<sub>o</sub>

$R^1$ -PhePhe-COO-PhePhe- $R^2$	I <sub>m</sub>
$R^1$ -Cyc-COO-Phe-COO-PhePhe- $R^2$	I <sub>n</sub>
$R^1$ -Cyc-CH <sub>2</sub> O-Phe-COO-PhePhe- $R^2$	I <sub>o</sub>

- 5 Above and below R<sup>1</sup> und R<sup>2</sup> denote preferably alkyl or alkoxy. In the compounds of the formula PheX denotes a 1,4-phenylen group substituted by an halogen atom, preferably by fluorine or alkoxy.

n preferabls is 1 or 2, particularly 1.

- 10 m preferabls is 0.

Above and below R<sup>1</sup> and R<sup>2</sup> each preferably denote alkyl with preferably 1 to 13 C atoms, particularly 3 to 12 C atoms wherein one or the two CH<sub>2</sub> groups may be replaced by -O- or -CO-.

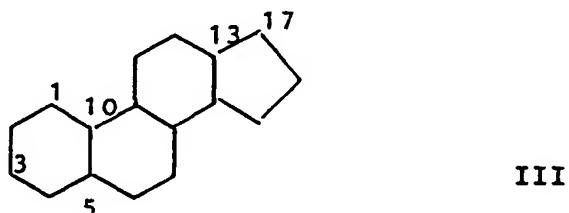
- 15 Preferably only one CH<sub>2</sub> group is replaced, particularly preferred by -O-.

- If R<sup>1</sup> and R<sup>2</sup> each are an alkyl radical wherein one ("alkoxy" or "oxaalkyl") or two ("alkoxyalkoxy" or "dioxaalkyl") nonadjacent CH<sub>2</sub> groups may be replaced by -O-, these radicals can be straight-chain or branched. Preferably, it is straight-chain and has 2, 3, 4, 5, 6, 7, 8, 9 or 10 C atoms and is accordingly preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, ethoxy, propoxy, butoxy, penyloxy, hexyl-oxy, heptyloxy, nonyloxy, decyloxy, also methyl, undecyl, dodecyl, tridecyl, tetradecyl, methoxy, undecyloxy, dodecyloxy, tridecyloxy or tetradecyloxy.

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- Oxaalkyl is preferably straight chain 2-oxapropyl (= methoxy-methyl), 2-(=ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl,
- 5 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, 1,3-dioxabutyl (= methoxymethoxy), 1,3-, 1,4-, 2,4-dioxapentyl, 1,3-, 1,4-, 1,5-, 2,4-, 2,5- or 3,5-dioxahexyl, 1,3-, 1,4-, 1,5-, 1,6-, 2,4-, 2,5-, 2,6-, 3,5-, 3,6- or 4,6-dioxaheptyl.
- 10 The chiral steroid esters of the formula II used according the invention are also known per se, for example Flüssig-kristalle in Tabellen, VEB Deutscher Verlag für Grundstoff-industrie, Leipzig Vol. I 1974 and Vol. II, 1984.

- 15 In the compounds of the formula II Ster denotes a saturated or unsaturated gonan-3-yl group of the formula III



- being preferably substituted in the 5-, 10-, 13- and/or 17-position by normal or branched alkyl residues with up to 10 C-atoms.
- 20 The compounds of the formula II wherein Ster denotes a cholesterolin-3-yl group are preferred.
- Furthermore preferred are those compounds of the formula II wherein Ster denotes a cholestan-3-yl group, a cholest-2-en-3-yl group, a sitosterin-3-yl group, an 17-alkylandrostan-3-yl group, an 17-alkylandrosten-3-yl group or an estron-3-yl group.
- 25

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The residue R<sup>3</sup> of the formula II preferably is an alkyl group with 1 to 18; preferably 2 to 10 C atoms.

- The inventive cholesteric liquid crystalline phases formed by the compounds of the formulae I and II preferably contain at least one preferably two or more non-chiral compounds of the formula I and at least one preferably two, three or more, chiral steroid esters of the formula II. Said cholesteric liquid crystalline phases contain about 5 20 to 90 preferably 40 to 75 % of one or more compounds of the formula I and about 10 to 80 preferably 25 to 10 60 % of one or more compounds of the formula II. In these cholesteric liquid crystalline phases the amount of the compound of the formula I and the amount of the compound of the formula II add up to 100 %.
- 15 The clearing point of these cholesteric liquid crystalline phases (Ch-I) lies preferably between 37 ° and 100 °C particularly preferred between 50 °C and 90 °C.
- 20 The cholesteric liquid crystalline phases used in the present invention are prepared in a manner which is customary per se. As a rule, the components are dissolved in one another preferably at elevated temperature.
- 25 Because of the good gloss and the low weight of the cholesteric liquid crystalline phases, only relatively small amounts thereof is required in the decorative composition. Although the absolute amount depends on the nature of the formulation and the desired coloured effect, as a rule about 5 to about 80 % by weight of the preferably 10 to 40 % are employed.
- 30 The cholesteric liquid crystalline phases may be micro-encapsulated before admixing to the vehicles.

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The microencapsulated cholesteric liquid crystalline phases are prepared in a manner which is customary per se (For example U.S. Patent 2,800,457).

Vehicles used for the formulations according to the invention are the substances customary for, for example, lipsticks, grease sticks, creams, powders and other cosmetics. These are known to the expert or are to be found in standard works, such as, for example, H. Janistyn, Handbuch der Kosmetika und Riechstoffe (Handbook of Cosmetics and Perfumes), Hüthig Verlag Heidelberg. Preferred vehicles are, for example, water based binders like polyvinyl alcohols or polyurethanes.

The formulations according to the invention contain as colouring constituents in each case at least one of the abovementioned cholesteric liquid crystalline phases formed by the compounds of the formula I and the compounds of the formula II.

Very attractive coloured effects are achieved. The present invention therefore provides very advantageous new decorative compositions with very attractive coloured effects and a very pleasant skin feeling.

The following examples are intended to illustrate the invention without limiting it. Percentages above and below are percentages by weight. All the temperatures are given in degrees Centigrade. The symbols are furthermore as follows: Cr: crystalline solid state, S: smectic phase (the index characterizes the phase type), N: nematic phase, Ch: cholesteric phase, I: isotropic phase. The figure between two symbols indicates the transition temperature.

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Example 1

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	49.3 %
5	p-pentylphenyl-p-hexyloxybenzoate	24.7 %
	cholesteryl nonanoate	11.7 %
	cholesteryl valerate	7.4 %
	cholesteryl propionate	6.9 %

exhibits a bright, red colour and Ch 52.3 ° I

10 Example 2

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	46.7 %
	p-pentylphenyl-p-hexyloxybenzoate	23.3 %
15	cholesteryl nonanoate	13.5 %
	cholesteryl valerate	8.6 %
	cholesteryl propionate	7.9 %

exhibits a bright, yellow colour and Ch 53.2 ° I

Example 3

20 A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	44.5 %
	p-pentylphenyl-p-hexyloxybenzoate	22.2 %

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cholesteryl nonanoate	15.0 %
cholesteryl valerate	9.5 %
cholesteryl propionate	8.8 %

exhibits a bright, green colour and Ch 53.9 ° I

5 Example 4

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

p-pentylphenyl-p-methoxybenzoate	41.0 %
p-pentylphenyl-p-hexyloxybenzoate	20.5 %
10 cholesteryl nonanoate	17.3 %
cholesteryl valerate	11.0 %
cholesteryl propionate	10.2 %

exhibits a bright, blue colour and Ch 55.6 ° I

Example 5

15 A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

p-pentylphenyl-p-methoxybenzoate	40.0 %
p-pentylphenyl-p-hexyloxybenzoate	20.0 %
cholesteryl nonanoate	18.0 %
20 cholesteryl valerate	11.1 %
cholesteryl propionate	10.6 %

exhibits a bright, blue colour and Ch 56 ° I

Example 6

25 A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

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	p-pentylphenyl-p-methoxybenzoate	38.0 %
	p-pentylphenyl-p-hexyloxybenzoate	19.0 %
	cholesteryl nonanoate	19.3 %
	cholesteryl valerate	12.3 %
5	cholesteryl propionate	11.4 %

exhibits a bright, purple colour and Ch 56.8 ° I.

Example 7

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

10	p-pentylphenyl-p-methoxybenzoate	18.0 %
	p-pentylphenyl-p-hexyloxybenzoate	16.0 %
	p-pentylphenyl-p-octyloxybenzoate	16.0 %
	cholesteryl valerate	25.0 %
	cholesteryl nonanoate	25.0 %

15 exhibits a bright colour and Ch 57.6 ° I.

The cholesteric liquid crystalline mixtures of the examples 1 to 7 are admixed to customary vehicles to achieve decorative compositions with attractive coloured effects and pleasant skin feeling.

20 Example 8

Decorative cosmetic composition formulation

25 A solution of Carbopol 940 (BF Goodrich Co, Cleveland, Ohio) at a solution of 0.25 % in water is neutralised with vigorous stirring to a pH 7.0 by careful addition of sodium hydroxide solution. A clear highly viscous gel is formed. By use of a nozzle, strands of chiral nematic

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liquid crystal (of example 1) are injected into the gel to obtain an attractive cosmetic formulation having an iridescent colour effect in the bulk sample, and a pleasant smooth feel when rubbed into the skin.

5      Example 9

Liquid crystal mascara formulation

The chiral nematic liquid crystal mixture of example 6 is incorporated into capsules of gelatin/gum arabic coacervate by the process of U.S. Patent 28,00,457 example 2,  
10 incorporating the optional hardening step described in example 1 of the same patent. The stirrer speed is adjusted to provide capsules of mean diameter 0.6 mm. The capsules are dispersed into a Carbopol gel obtained as above at a concentration of 5 % to obtain a clear mascara  
15 which imparts iridescent highlights to the eyelash.

Example 10

Iridescent decorative Coating

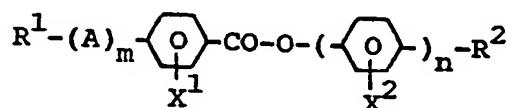
The chiral nematic liquid crystal mixture of example 3 is microencapsulated in a gelatin/gum arabic coacervate system to yield capsules of mean diameter 10  $\mu\text{m}$ . The aqueous capsule slurry is filtered from excess water and incorporated in a solution of polyvinyl alcohol to yield a final liquid crystal content of 20 % and PVA content of 8 %. The resulting viscous slurry is applied  
20 by screenprinting through a mesh of 70 threads per centimetre to a black board, and after drying imparts an attractive iridescent colour effect.  
25

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**Decorative Composition****Claims**

1. A decorative composition comprising in admixture:

a) one or more non-chiral compound of the  
5 formula I

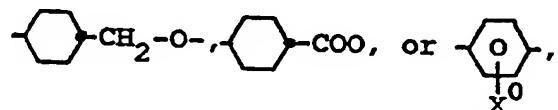


wherein

10  $R^1$  and  $R^2$  are each independently a normal or branched alkyl or alkenyl residue with up to 16 C atoms wherein one or two nonadjacent  $\text{CH}_2$  groups of these residues may be replaced by -O- or -CO-

15

A denotes a group of the formula

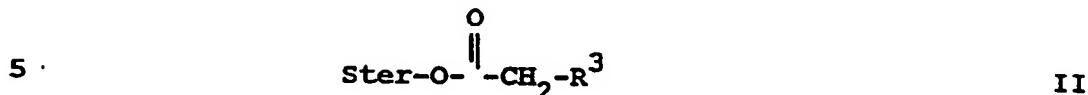


$X^0$ ,  $X^1$  and  $X^2$  are each independently hydrogen or an halogen atom,

m is 0 or 1, and

n is 1 or 2,

- b) one or more chiral steroid ester of the formula II



wherein

R<sup>3</sup> is a normal or branched alkyl or  
alkenyl residue with up to 16 C atoms  
wherein one CH<sub>2</sub> group may be replaced  
by -O-, -O-CO- or -CO-O-, and

10

Ster denotes a saturated or unsaturated  
gonan-3-yl group being optionally sub-  
stituted by up to 6 normal or branched  
alkyl residues with 1 to 10 C atoms,  
and

15

- c) at least one vehicle and, if desired, at least  
one auxiliary.

2. Composition according to Claim 1 characterized in  
that m is 0 and n is 1 in formula I.

20 3. Composition according to Claim 1 or 2 characterized  
in that Ster denotes a cholesterin-4-yl group.